

# A sand composite with surface gel coating containing alkylamine toward the removal and immobilization of complex metal ions from electroplating wastewater

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## ABSTRACT

SiO<sub>2</sub> gel was formed on the grain surface of silica sand by hydrolysis and condensation of tetraethyl orthosilicate in water with the addition of 1-butylamine. The resultant product was a composite consisting of sand grains with mesoporous silica coating containing alkylamine inside.

This composite exhibited basicity in the wastewater from copper electroplating due to its release of amine. As a result, the strongly acidic wastewater was neutralized and the co-precipitation of complex metal ions occurred. It was shown that up to 12 major metal ions in the wastewater could be simultaneously removed under static condition at room temperature by using the sand composite. The Fe and Cu in the wastewater could be removed completely, while the concentrations of Al, Cd, Ti, V, and Zn in the wastewater were reduced by two to three orders of magnitude. After the removal of multiple metal ions from the electroplating wastewater, the used sand was further applied as a raw material for making a silicate glass. The glass was chemically stable and thus the heavy metal ions from the wastewater were immobilized.

**Key words** | copper electroplating wastewater, glass, immobilization, removal of metal ions, sand composite

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## INTRODUCTION

Heavy metal ions in wastewater are increasing with the industrial development (Paul 2017). These metal ions mainly originate from electroplating (Hang *et al.* 2009), textile and chemical industries (Yang *et al.* 2018). The heavy metal ion contaminants usually cannot be degraded into harmless species (Adrees *et al.* 2015) before entering our food chains via irrigation, soil, and drinking water. In recent years, the removal of heavy metal ions from wastewaters is becoming one of the most important environmental challenges that investigators are facing (Baydarashvili *et al.* 2017). The current objectives of wastewater treatment include the removal of contaminants and the conversion of contaminants into harmless and stable substances in order to reduce or eliminate the toxicity caused by the pollutants (Carolin *et al.* 2017). Besides, the alteration of acidity or alkalinity of wastewaters to be close to neutral state is also an important task (Blodau 2006; Macaskie *et al.* 2007).

Common methods for removing metal ions from wastewaters include chemical precipitation, flocculation, ion

exchange, reverse osmosis, electro-dialysis, membrane filtration and adsorption (Fu & Wang 2011). Among these methods, flocculation is an industrial route to treat heavily contaminated water (Yang *et al.* 2013). In this method, flocculants are used to cause the coagulation of metal ions. Both organic (such as N-(2-carboxyethyl), chitosans (Bratskaya *et al.* 2009), polyvinylamine (Huang *et al.* 2016) and inorganic flocculants (such as alum (Pang *et al.* 2011) have been widely used as flocculants. After the flocculation has processed, suspended flocculates or resultant precipitates are formed and separated from the treated water mainly by pressure filtration. Besides by coagulation, precipitation can also be induced by chemical reactions between the heavy metal ions and the precipitants, such as hydroxide compounds, and sulfate (Hamdona *et al.* 1993; Soylak & Murat 2014). Since precipitants are strongly case-sensitive to metal ions and the precipitation reactions are pH-dependent, it is of much importance to choose an appropriate precipitant. Adsorption is another widely used

method for removing metal ions with low concentrations in wastewaters (Fu & Wang 2011). Highly efficient and low-cost adsorbents are important in the current practice. Most of the above-mentioned methods have the advantage of simple operation. However, they lead to the formation of flocs, sludges or spent adsorbents, which contain the toxic metal ions and generate secondary pollution (Fu & Wang 2011).

Sand has long been used in water purification and is the main raw material in the production of silicate glasses. Inspired by this fact, our group turned its attention to developing a sand-based precipitant, expecting that it would remove metal ions by precipitation. More importantly, it will not produce secondary pollutants as the generated sludge containing the used sand and the formed precipitates would be vitrified, as reported in our previous works (Li *et al.* 2013; Liu *et al.* 2017). Herein, a new precipitant for wastewater treatment was synthesized using silica sand, tetraethyl orthosilicate (TEOS), and 1-butylamine. Quick hydrolysis and condensation of TEOS in alkylamine solution led to the formation of silica gel coating on the surface of sand grains. The product was a composite consisting of porous silica-amine coating on a sand core, which showed precipitation effect when the amine was released into a copper electroplating wastewater. Under static condition, the sand composite could effectively remove 12 types of metal ions in the wastewater. In the meantime, the pH of the wastewater was lowered to neutrality. In addition, the used sand composite mixed with the precipitated metal ions was successfully used as a raw material to make CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass. As a result, the complex heavy metal ions from the copper electroplating wastewater were stably immobilized in the prepared glass.

## METHODS AND METHODOLOGY

### The preparation of sand composite

The raw sand (R-sand) was the standard sand used in the cement and concrete industry. Other reagents were of analytic grade. The sand composite was prepared as follows. Sand (210 g) and distilled water (135 ml) were mixed under vigorous mechanical stirring (250–300 rpm) in a high-speed mixer for 2 min followed by the successive additions of 100 ml of 1-butylamine and 135 ml of TEOS. Stirring was continued in the mixer for two minutes. The hydrolytic poly-condensation reaction of TEOS under amine catalysis resulted in the formation of SiO<sub>2</sub> gel on the surface of the sand grains. The collected sample was

dried in an oven at 80 °C for 4 h. The resultant product was a sand composite. After having been cooled down to room temperature, it was directly used to treat the wastewater from copper electroplating.

### The treatment of the wastewater

The wastewater from copper electroplating was taken from a local electroplating plant. Its chemical composition was analyzed and is listed in Table 1 (in the Discussion section). The main components in the wastewater were Fe and Cu. The other elements were either from metal objects or from electroplating solution. The initial pH level of the wastewater was 1.9. The treatment of the wastewater was performed under static condition at room temperature.

**Table 1** | Concentrations of elements in the original electroplating wastewater and the treated water, measured by the ICP method

Element	Concentration in original waste water (ppm)	Concentration in neutralized water (ppm)
Fe	4,549.3	2.1214
Cu	153.8	0.135
Cr	0.1892	0.0036
Pb	0.2212	0.011
Cd	0.043	0.0004
Zn	19.308	0.0776
V	0.6538	0.0001
Mn	18.7	5.5391
Ni	2.039	3.6789
P	1.7558	0.387
B	2.4505	0.1328
Rb	0.0869	0.107
Zr	0.0647	0.0017
Sr	0.9819	1.118
Ti	1.9516	0.0018
Co	2.1118	0.1213
Al	5.4871	0.013
Ir	0.0413	0.0048
K	5.3246	40.441
Mg	84.159	106.6
Ca	170.1	200
Si	6.6839	27.976
Na	163.5	213.8
S	3,583.9	4,690.7

The aim was to precipitate multiple metal ions as well as to neutralize the pH of the wastewater. In this approach, 100 ml of wastewater was first diluted with 50 ml of water before 160 g of the coated sand was added. The mixture was placed without stirring for up to 101 h until its pH was close to 7.

### Preparation of the glass sample

The sand composite after the wastewater treatment was collected by pouring out the treated water, followed by drying at 110 °C. Then, it was used as the component of SiO<sub>2</sub> to make a glass with the main composition of 40.8SiO<sub>2</sub>-7.2Al<sub>2</sub>O<sub>3</sub>-19.2CaO-12.8MgO-20Fe<sub>2</sub>O<sub>3</sub> (wt%). Other starting materials in the glass batch included the reagents of Al(OH)<sub>3</sub>, CaCO<sub>3</sub>, MgO and Fe<sub>2</sub>O<sub>3</sub>. In addition, as required by the glass melting, Sb<sub>2</sub>O<sub>3</sub> and NaNO<sub>3</sub> were added as refining agents, and CaF<sub>2</sub> as the fluxing agent. The glass batch was melted in an alumina crucible at 1,500 °C in an electric furnace for 3 h. The melt was poured out and shaped in a steel mold. The glass sample was then annealed at 500 °C for 1 h.

### The PCT test of the prepared glass

Product Consistency Test (PCT) has been conducted following the standard ASTM C 1285-14 (ASTM 1998) to evaluate the stability of the prepared glass and the leaching of metal ions in solution. In the test, 1.5 g of glass particles sized 75–150 μm were put into 15 ml of deionized water as leachant solution. Three parallel tests were carried out at 90 °C for 7 days. The leachate was then filtered and analyzed by inductively-coupled plasma optical emission spectroscopy (ICP-OES). The data were normalized by comparing the blank solution.

The normalized elemental mass release,  $ri$ , was calculated from Equation (1) (ASTM 1998):

$$ri = \frac{Ci}{fi(SA/V)} \quad (1)$$

where  $ri$  is the normalized elemental mass release (g/m<sup>2</sup>);  $Ci$ , concentration of element 'i' in the solution (g/m<sup>3</sup>);  $fi$ , mass fraction of element 'i' in the original sample; and  $SA/V$  (m<sup>-1</sup>), the ratio of the sample surface (SA, m<sup>2</sup>) area to the leachate volume (m<sup>3</sup>). The nominal composition of glass was used to calculate  $fi$ . The density of the glass is 2.81 g/cm<sup>3</sup>. Supposing that the particles are spherical with an average size of 112 μm,  $SA/V$  equals 1,906 m<sup>-1</sup>.

### Characterizations

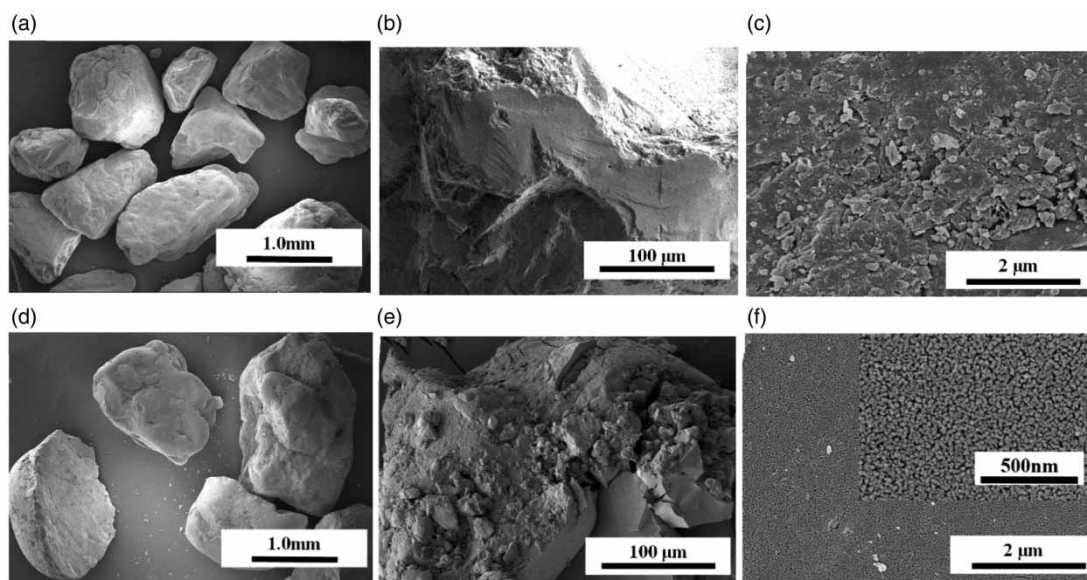
The surface morphology of sand and its composite was observed under a field-emission scanning electron microscope (SEM, Hitachi SU8020, Japan). N<sub>2</sub>-sorption measurements were performed at 77 K on an Autosorb-iQ-C adsorption apparatus (Quantachrome Instruments, USA). The surface area was calculated based on the Brunauer-Emmett-Teller (BET) model and the pore size distribution (PSD) curve was determined based on the Barrett-Joyner-Halenda (BJH) model with the adsorption data of the isotherm. The Fourier transform infrared (FTIR) spectrum of the sample was recorded on a Nicolet iS10 Spectrometer (Thermo Fisher Scientific, USA) in the wave number range of 400–4,000 cm<sup>-1</sup> with KBr slice containing sample powder. The concentrations of elements in the wastewater were analyzed with an inductive coupled plasma emission spectrometer (Agilent-ICPOES730, USA). For each test, 1 ml of wastewater was put in a clean Teflon beaker, then 3 ml of nitrohydrochloric acid was added. The mixture was heated at 150 °C for 10 min. Finally, it was cooled down and diluted with ultrapure water to a total volume of 10 ml for the measurement. Thermogravimetry (TG) analysis was performed on the sand composite using a Pyris6 TG analyzer (USA) with an empty alumina as the reference and ramp rate of 10 °C/min.

## RESULTS AND DISCUSSION

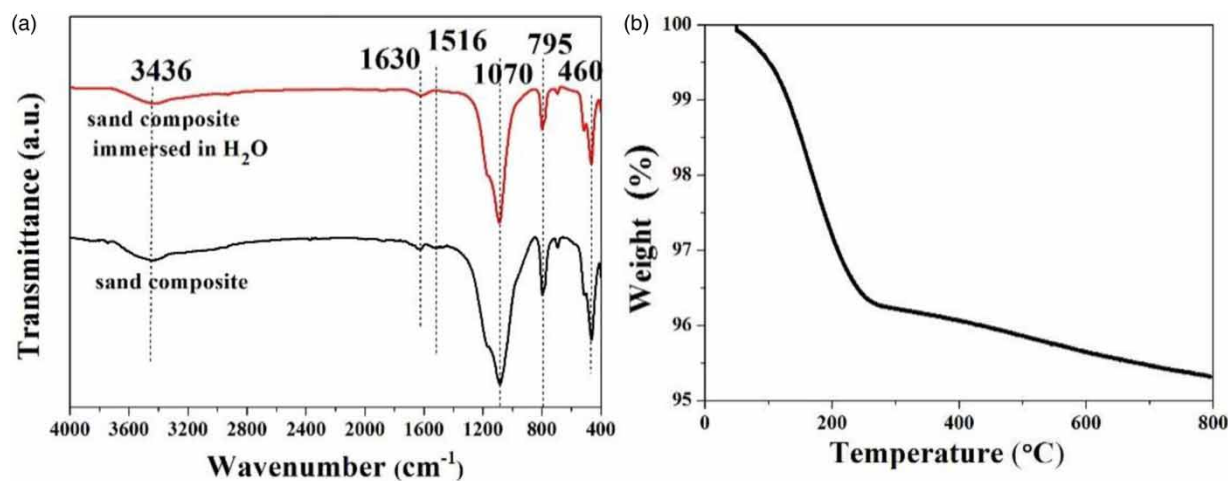
### Characterization of the sand composite

Figure 1 shows the surface morphology of the grains of R-sand and sand composite. The images with the lower magnification (Figure 1(a) and 1(d)) do not show significant difference among the irregularly shaped sand grains before and after the silica gel coating. However, under a higher magnification, the smooth surface of the R-sand grain contrasts with the much rougher surface of the grains of sand composite (Figure 1(b) and 1(e)). The images with higher magnification in Figure 1(c) and 1(f) reveal that the surface of R-sand has randomly distributed large particles, while the composite sand grain surface is covered by relatively homogeneous coating. The inset in Figure 1(f) shows that the surface coating is composed of spherical nanoparticles with inter-particle voids, suggesting a porous structure of the coating.

The FTIR spectrum of the prepared sand composite is shown in Figure 2(a). The bands at 1,070, 795 and 460 cm<sup>-1</sup> are attributed to the vibrations of V<sub>as</sub>(Si-O-Si),



**Figure 1** | The SEM images of the R-sand (a)–(c) and the prepared sand composite (d)–(f).



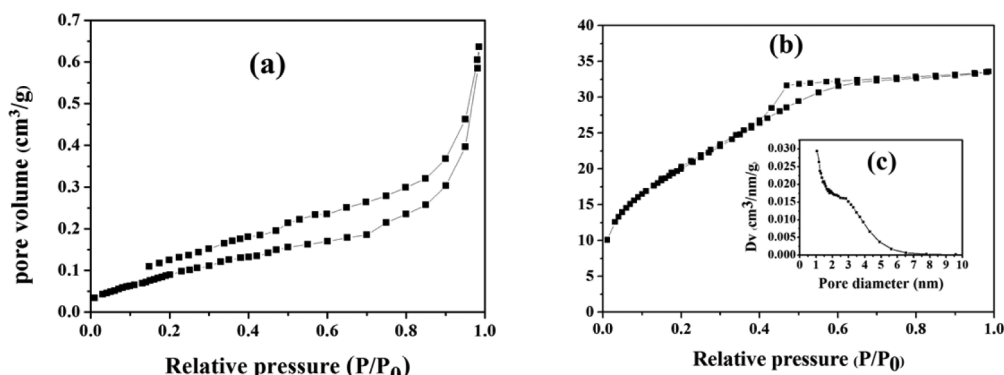
**Figure 2** | FTIR spectrum (a) and TG curve (b) of the sand composite.

$V_s(\text{Si-O-Si})$  and  $\delta(\text{Si-O-Si})$  (Shahata 2011; Wamba *et al.* 2018), respectively. These Si-O-Si bonds are not only related to the silica skeleton of R-sand but also to silica gel coating on the grain surface. The band at  $1,516\text{ cm}^{-1}$  is caused by the N-H bending vibration of  $\text{NH}_2$  groups, which were traced to the butylamine used in the synthesis (Jing *et al.* 2016). The bands at  $1,630$  and  $3,436$  are ascribed to OH groups and adsorbed water molecules (Thamaraiselvi & Kalpanadevi 2012; Fotoohi & Mercier 2015). The TG curve of the sand composite is shown in Figure 2(b), which indicates a total weight loss of 4.7% up to  $800^\circ\text{C}$ . The weight loss of

4.2% between  $100$  and  $800^\circ\text{C}$  was mainly due to the removal of the confined butylamine in the sand composite upon heating, while the rest was the loss of adsorbed water in the composite (Kong *et al.* 2016). After the sand composite (16 g) was immersed in distilled water (10 ml), the FTIR spectrum of the collected and dried sand shows the disappearance of the band correspondent to the N-H bending vibrations of  $\text{NH}_2$  groups (Figure 2(a)), suggesting the release of butylamine from the sand composite into water.

The  $\text{N}_2$ -sorption isotherms of the R-sand and the sand composite are shown in Figure 3. The R-sand shows a type II





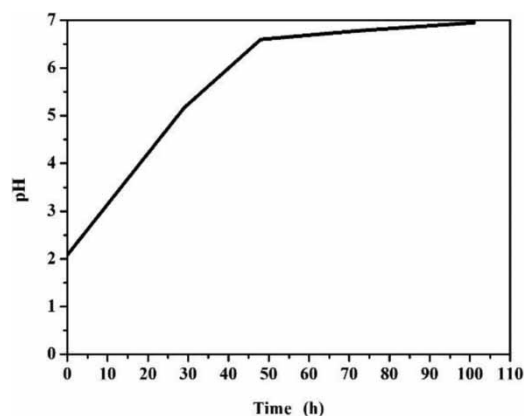
**Figure 3** |  $N_2$ -sorption isotherms of the R-sand (a), the prepared sand composite (b) and the pore size distribution curve of the sand composite (c).

isotherm (Figure 3(a)) with a very small adsorption capacity, indicating that the R-sand is not porous. Its adsorption and desorption branches are not closed, mainly due to its small surface area, which is only  $0.32 \text{ m}^2/\text{g}$ . As can be seen from Figure 3(b), the isotherm of the sand composite is of type IV with an H2 type hysteresis loop, indicating that the composite has mesopores with different shapes and sizes (Rouquerol *et al.* 1999). The surface area was determined to be  $73.5 \text{ m}^2/\text{g}$ , which is 230 times that of the R-sand. The BJH-based PSD curve in the inset in Figure 3(b) shows that the main pore size was 2.83 nm. These mesopores originated from the interparticle voids of the formed gel particles on the sand grain surface.

The above SEM, FTIR, TG and  $N_2$ -sorption results indicate that the synthesized product is a composite consisting of silica sand as the core and a porous butylamine-silica coating on the grain surface.

### Water treatment under static condition

As mentioned earlier, the pH of copper electroplating wastewater was 1.9. Even after it had been diluted by distilled water (at 100:50), it still maintained a pH value of 2.08. This implies that its emission to a water stream would greatly increase the acidity. Upon the addition of the sand composite in the diluted wastewater, the pH of the water increased due to the release of butylamine from the sand composite. As shown in Figure 4, the pH of wastewater first increases to 6.6 at 48 h, then slowly approaches 6.95 at 101 h, suggesting that the release of amine from the sand composite was non-linear with time. Increasing the dilution or/and the dosage of sand composite would greatly hasten the neutralization process. For example, when 200 ml of diluted wastewater (at 1:1) was treated with 180 g of sand composite, the pH of the treated water reached 7.16 at 48 h. In this case, it was noted that the



**Figure 4** | Time-dependent pH variation of the treated water.

pH of wastewater continued to rise to 7.33 and 7.89 if prolonging the time to 72 h and 101 h. Therefore, it is necessary to terminate the neutralization process when the pH of wastewater reaches the vicinity of 7. The sand composite can be separated and collected for reuse in the next run till its amine is used up.

Table 1 shows the ICP elemental analysis results of the original wastewater and the neutralized water. The data indicate that the concentrations of Fe and Cu as the main components in the original wastewater were greatly reduced after the treatment, resulting in removal efficiencies of more than 99.9%. Except Ni, other heavy metal ions including Cd, Co, Cr, Mn, Pb, V, Zn and Zr also show great reduction in concentrations after the treatment. The concentrations of Al, Cd, Ti, V, Zn have also been reduced by two or three orders of magnitude, corresponding to removal efficiencies of 95–100%.

Except that the removal efficiency of Mn is 70%, the efficiencies for others were more than 94%. Among these

ions, the hydroxides of  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ti}^{4+}$  have solubility constants ( $K_{sp}$ ) on the orders of magnitude of  $10^{-20}$  to  $10^{-40}$ . Although  $\text{Zn}(\text{OH})_2$ ,  $\text{Cd}(\text{OH})_2$ ,  $\text{Mn}(\text{OH})_2$ , and  $\text{Co}(\text{OH})_2$  have larger  $K_{sp}$  ( $10^{-13}$  to  $10^{-17}$ ) than the above hydroxides (Reichle *et al.* 1975), the correspondent metal ions also tend to precipitate under the basic condition. Therefore, it is reasonable to deduce that these ions were removed by chemical precipitation (Liu *et al.* 2013). Besides, other elements like P, B in the wastewater also decrease. They existed in the wastewater as anions and were probably removed by the adsorption on the sand composite with a large surface area (see the  $\text{N}_2$ -sorption result) (Kargar-Razi & Yahyaabadi 2012). However, we also noted that the concentrations of Si, Ca, Mg and Na, K increased. This may be due to the dissolution of fine particles on the surface of the sand grains (see Figure 1(c)) under the local basic environment generated by the released amine. In addition, the increases of Ni and S after the treatment are not fully understood at the moment.

The above results demonstrate that the prepared sand composite could simultaneously remove the vast majority of metal ions in the complex copper electroplating wastewater. The advantage of this approach is its wide validity to remove metal ions with concentrations varying in orders of magnitude; at the same time, the strongly acidic wastewater was successfully neutralized.

### The stability of glass and the leaching of the immobilized metal ions

The normalized element release of the prepared glass is indicated by the values of  $r_i$  ( $i = \text{Ca, Mg, Fe, Al, Si}$ ), which are  $r_{\text{Ca}} = 0.11$ ,  $r_{\text{Mg}} = 0.004$ ,  $r_{\text{Fe}} = 3 \times 10^{-6}$ ,  $r_{\text{Al}} = 4 \times 10^{-4}$  and  $r_{\text{Si}} = 0.11$ . The results are presented in Figure 5. Since the

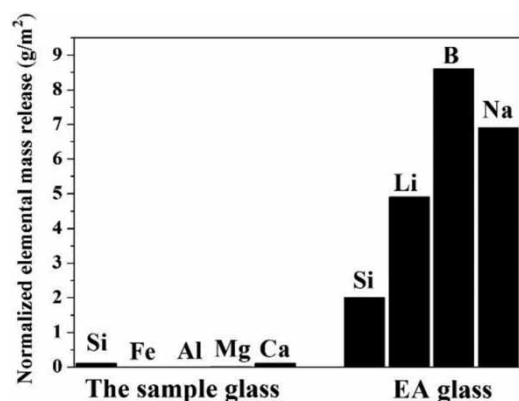


Figure 5 | Comparison of the normalized elemental mass release ( $\text{g}/\text{m}^2$ ) of the prepared glass and the environmental assessment glass.

Table 2 | Concentrations of major elements released from the glass in the PCT test

Element	Concentration in solution from the PCT test (ppm)
Fe	0.0008
Cu	Undetectable
Cd	0.0004
Co	0.0018
Cr	Undetectable
Mn	0.0022
Pb	0.0008
V	Undetectable
Zn	0.0098
Zr	0.0001
Al	0.0267
Ti	Undetectable

environmental assessment (EA) glasses specified in the PCT protocol are borosilicate glasses containing Li and Na, the normalized elemental mass release,  $r_{\text{B}}$ ,  $r_{\text{Li}}$  and  $r_{\text{Na}}$  in the EA glass are also shown in Figure 5. It is seen that the  $r_{\text{Si}}$  is only  $0.11 \text{ g}/\text{m}^2$ , about 20 times smaller than that of EA glass ( $r_{\text{Si}} = 2.0$ ) (Day *et al.* 1998; Kim *et al.* 2003). Therefore, it can be concluded that the glass, prepared from the used sand containing the metal ions from electroplating wastewater, was much more stable than the EA glass.

Since the precipitate containing the metal ions from the electroplating wastewater was mixed with the used sand, the metal ions were brought into the prepared glass. Table 2 shows the concentrations of the afore-mentioned 12 metal ions in the solution left from the PCT test. It is seen that all 12 elements have very low concentrations or are undetectable in the leached solution, suggesting that those metal ions from the electroplating wastewater were stably immobilized in the prepared glass.

### CONCLUSIONS

A sand composite with porous silica-amine coating on the surface was prepared and used to treat copper electroplating wastewater. It could release amine into solution, generating a basic environment. The strongly acidic wastewater thus was successfully neutralized by the added sand composite under static condition. In the meantime, 12 metal ions with high concentrations in the wastewater were simultaneously and effectively removed via the precipitation.

The used sand composite together with the precipitate was then directly used as a raw material for preparing chemically stable glass, in which the toxic metal ions were fully immobilized.

## ACKNOWLEDGEMENTS

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